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TEMPERATURE PROGRAMMABLE INJECTION TECHNIQUES FOR EXPLOSIVES

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14. ABSTRACT

Temperature programmable injection ports promise great versatility, capable of normal split/splitless injections and offering options to inject thermally labile materials with gentle heating profiles. Nitroaromatic and nitramine compounds useful in explosive formulations tend to be thermally labile and limited in volatility. Although LC/MS techniques have been proposed for analysis of these chemicals, GC and GC/MS techniques remain more convenient and more cost effective than LC/MS, and more sensitive than conventional LC analyses for nitroaromatics and nitramine explosives. ECD and other specialized GC detectors have also been described for the detection and analysis of nitroaromatics and nitramines, and these techniques offer additional options for the inexpensive analysis of explosives. All GC based techniques share the common challenges of vaporizing these compounds without excessive losses due to sorption and thermal reactivity. This report will describe results of an investigation to develop GC/MS analyses for nitroaromatics and nitramines, such as TNT and RDX, using a commercially available single-quadrupole GC/MS system with provision for positive and negative ion detection, EI and CI ionization conditions, and a programmable temperature vaporization (PTV) injection port. Conditions investigated include simple split/splitless injections, temperature programmed injections, and injections onto wide-bore pre-columns. GC/MS conditions investigated included electron impact and chemical ionization, using methane as reagent gas. Positive and negative CI conditions were investigated.

15. SUBJECT TERMS

gas chromatography, gas chromatography/mass spectrometry, chemical ionization MS

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Temperature Programmable Injection Techniques for Explosives

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Abstract

Keywords: Gas Chromatography, Gas Chromatography/Mass Spectrometry, Chemical Ionization MS

Temperature programmable injection ports promise great versatility, capable of normal split/splitless injections and offering options to inject thermally labile materials with gentle heating profiles. Nitroaromatic and nitramine compounds useful in explosive formulations tend to be thermally labile and limited in volatility. Although LC/MS techniques have been proposed for analysis of these chemicals, GC and GC/MS techniques remain more convenient and more cost effective than LC/MS, and more sensitive than conventional LC analyses for nitroaromatics and nitramine explosives. ECD and other specialized GC detectors have also been described for the detection and analysis of nitroaromatics and nitramines, and these techniques offer additional options for the inexpensive analysis of explosives. All GC based techniques share the common challenges of vaporizing these compounds without excessive losses due to sorption and thermal reactivity. This report will describe results of an investigation to develop GC/MS analyses for nitroaromatics and nitramines, such as TNT and RDX, using a commercially available single-quadrupole GC/MS system with provision for positive and negative ion detection, EI and CI ionization conditions, and a programmable temperature vaporization (PTV) injection port. Conditions investigated include simple split/splitless injections, temperature programmed injections, and injections onto wide-bore pre-columns. GC/MS conditions investigated included electron impact and chemical ionization, using methane as reagent gas. Positive and negative CI conditions were investigated.

Introduction

- Explosive analysis and detection techniques are critical to support environmental cleanups and provide enhanced security
- Liquid chromatography can analyze for most explosives, but the sensitivity is an issue
- Ion mobility spectrometry is rapid, reasonably sensitive, and compact but lacks verification
- Gas chromatography is applicable to volatile and semivolatile explosives, it requires a carrier gas, it can provide verification when combined with mass spectrometry
- Laboratory techniques find little use in security due to the response times, but their use can enhance the development of rapid-response sensing devices

Introduction - Continued

- Injection is critical to analysis of explosives
  - Must volatilize poorly volatile explosives
  - Must not promote degradation of thermally labile compounds
- Temperature programmable volatilization (PTV)
  - Offers a wide range of temperatures
  - Simile on-column injections

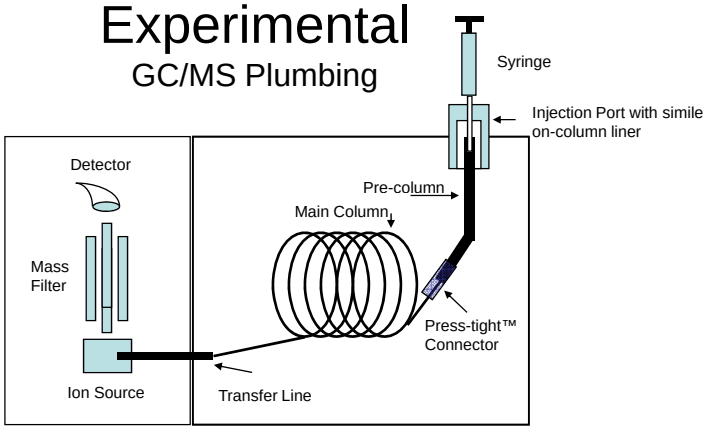
Experimental

Apparatus

- Thermo Electron Trace-DSQ GC/MS System
  - PTV and split/splitless injectors
  - Positive and negative ion detection
  - EI and CI ionization
- EPA Method 8330 Analytes
- Fused silica capillary column, 10 m X 0.25mm ID coated with 0.4 μm DB-5
- 1m X 0.53mm ID pre-columns – studied effect of coating thickness

Experimental

GC/MS Plumbing



Studied “simile on-column” injections, made onto a short (1-m) pre-column attached between the analytical column and the injection port. A special injection port liner (Thermo PN 453 220 52) served as a needle guide to align the injection needle and guide it into the entrance of the pre-column. Injection port programming allowed a “cold” injection. The column and pre-column were joined with deactivated press-tight™ (Restek, Inc) fittings.

Experimental

- Injection Size
- Pre-column – coated vs. uncoated
- Ion Volume Effects for CI

Experimental

Pre-column Choices

- Deactivated fused silica – 0.53mm ID, 1m long, deactivated for intermediate compounds
- 1m section of Restek RTX-TNT column (0.53mm ID, coated with 1.5μm RTX-TNT phase)
- 1m sections of wide-bore capillary column, 0.53mm ID coated with RTX-5 stationary phase – 0.5μm, 1.0μm, 1.5μm phase thickness

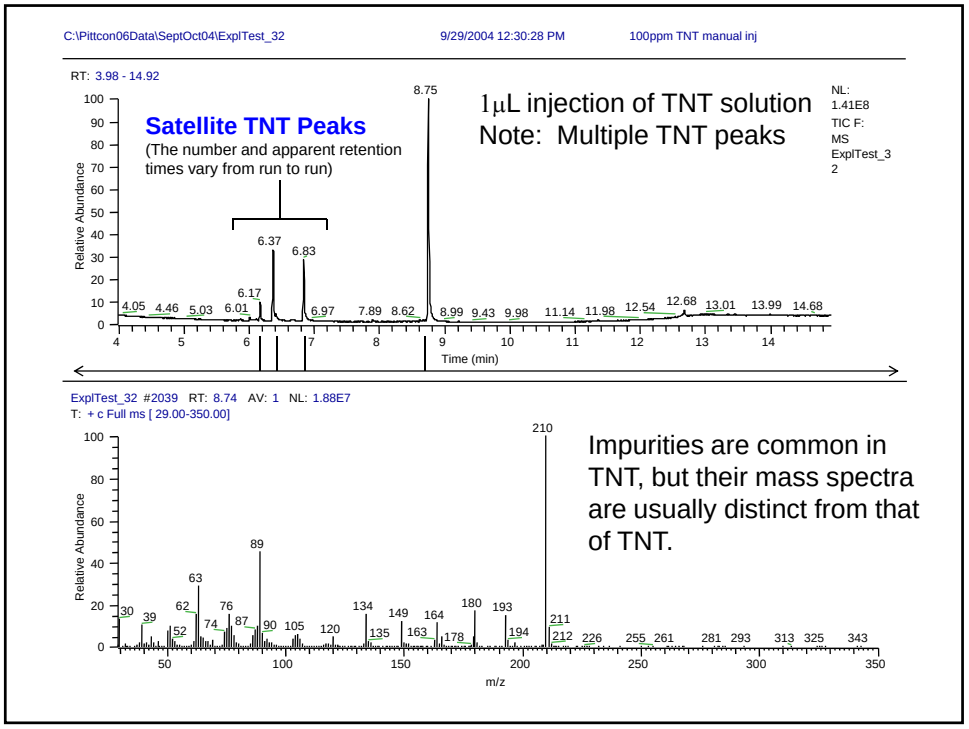
Experimental

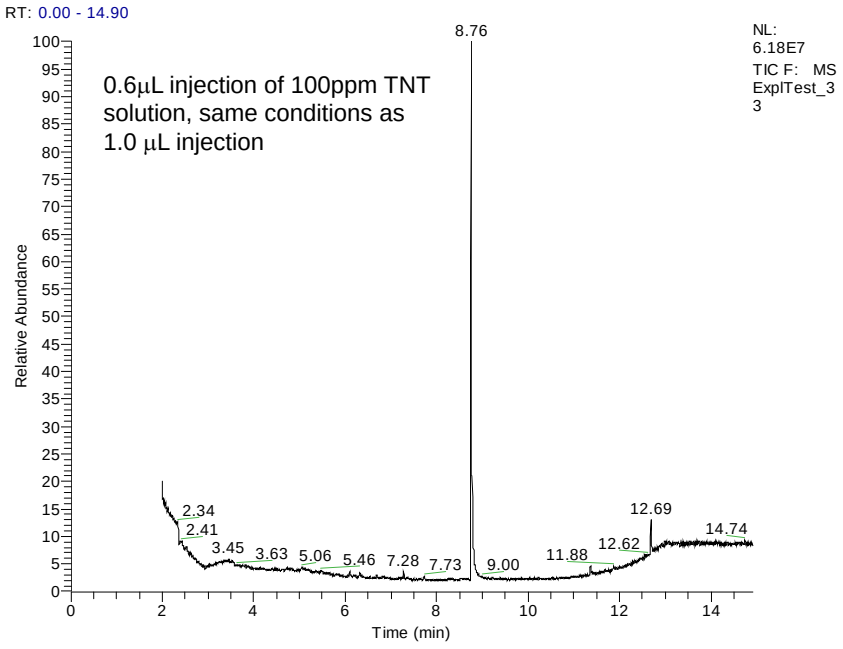
Analytes of Interest

Peak Number	Analyte	Peak Number	Analyte
1	Nitrobenzene (NB)	9	2,4,6-Trinitrotoluene (TNT)
2	2-Nitrotoluene (2-NT)	10	1,3,5-Trinitrobenzene (TNB)
3	3-Nitrotoluene (3-NT)	11	Hexahydro-1,3,5-trinitro-s-triazine (RDX)
4	4-Nitrotoluene (4-NT)	12	4-Amino-2,6-Dinitrotoluene (4-AM-DNT)
5	Nitroglycerine (NG)	13	3,5-Dinitroanaline (3,5-DNA)
6	2,6-Dinitrotoluene (2,6-DNT)	14	2-Amino-4,6-Dinitrotoluene (2-AM-DNT)
7	1,3-Dinitrobenzene (DNB)	15	N-Methyl-N,2,4,6-tetranitroaniline (Tetryl)
8	2,4-Dinitrotoluene (2,4-DNT)		

Injection Size

- Initial injection size was 1μL
- Chromatograms showed many more peaks than were expected
- Each analyte mass spectrum showed up in multiple peaks
- “Satellite Peaks” occurred under a variety of injection ramps and pressure conditions
- Satellite peaks disappeared when the injection size was reduced to $0.6\mu L$

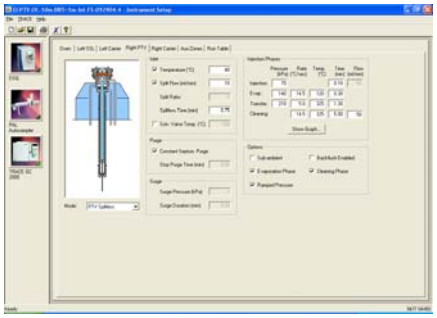

C:\Pittcon06Data\SeptOct04\ExplTest_32
9/29/2004 12:30:28 PM
100ppm TNT manual inj
RT: 3.98 - 14.92
Satellite TNT Peaks
(The number and apparent retention times vary from run to run)
1μL injection of TNT solution
Note: Multiple TNT peaks
NL: 1.41E8
TIC F: MS ExplTest_32
Relative Abundance
Time (min)
ExplTest_32 #2039 RT: 8.74 AV: 1 NL: 1.88E7
T: + c Full ms [29.00-350.00]
Impurities are common in TNT, but their mass spectra are usually distinct from that of TNT.
m/z


RT: 0.00 - 14.90
0.6μL injection of 100ppm TNT solution, same conditions as 1.0 μL injection
NL: 6.18E7
TIC F: MS ExplTest_33
Relative Abundance
Time (min)

Selected GC/MS Conditions

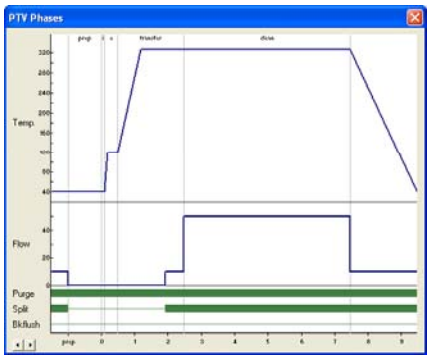
- MS scanned from 29 – 350 Dalton
- Ion source: 225°C
- Oven Program: 2 steps
  - 40°C(2.5min)-100°C@60°C/min(no hold)
  - 300°C(1.0 min)@25°C/min
- Transfer Line: 300°C

Injection Port Program



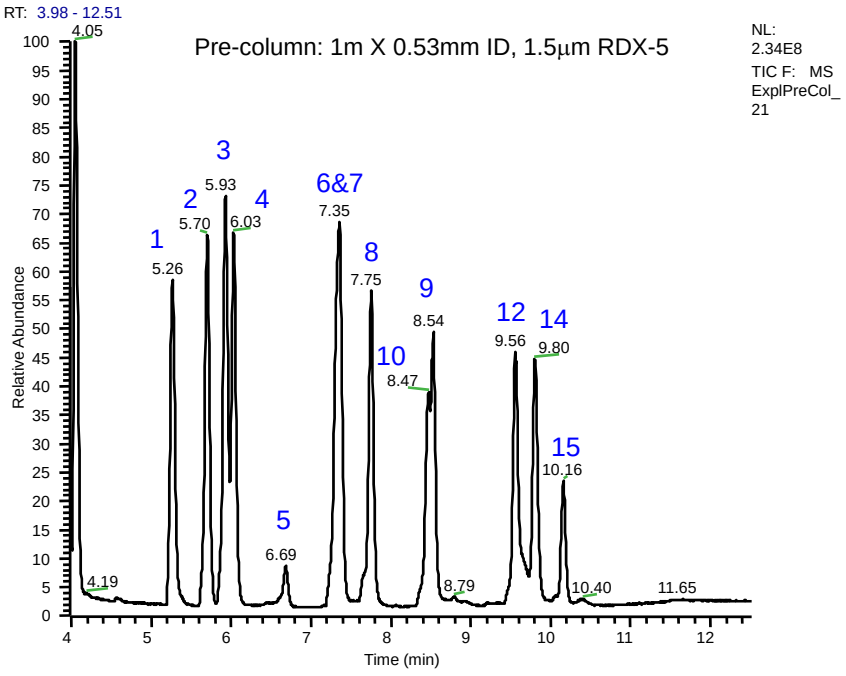
Temperature, Pressure, and Flow Conditions from XCalibur Software

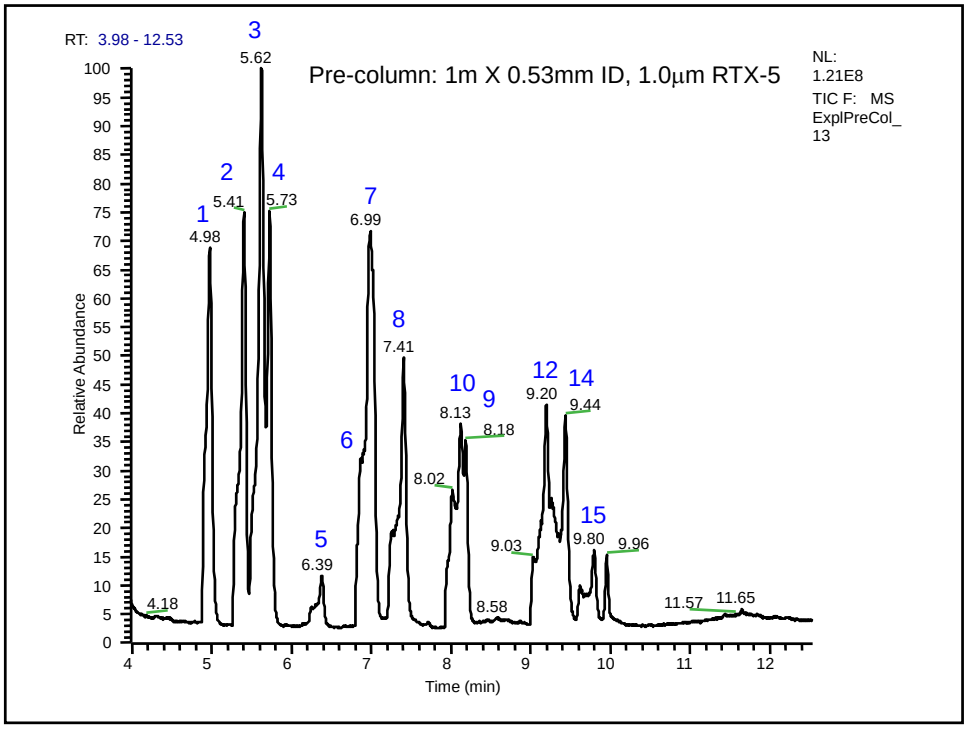
Temperature, Pressure, and Flow Plot

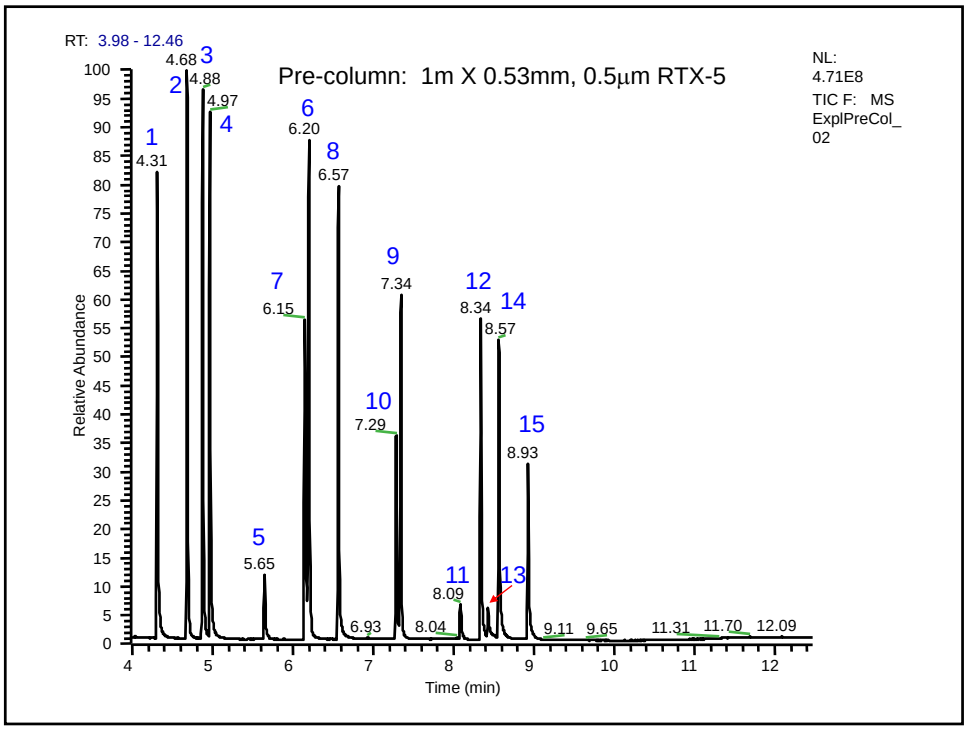


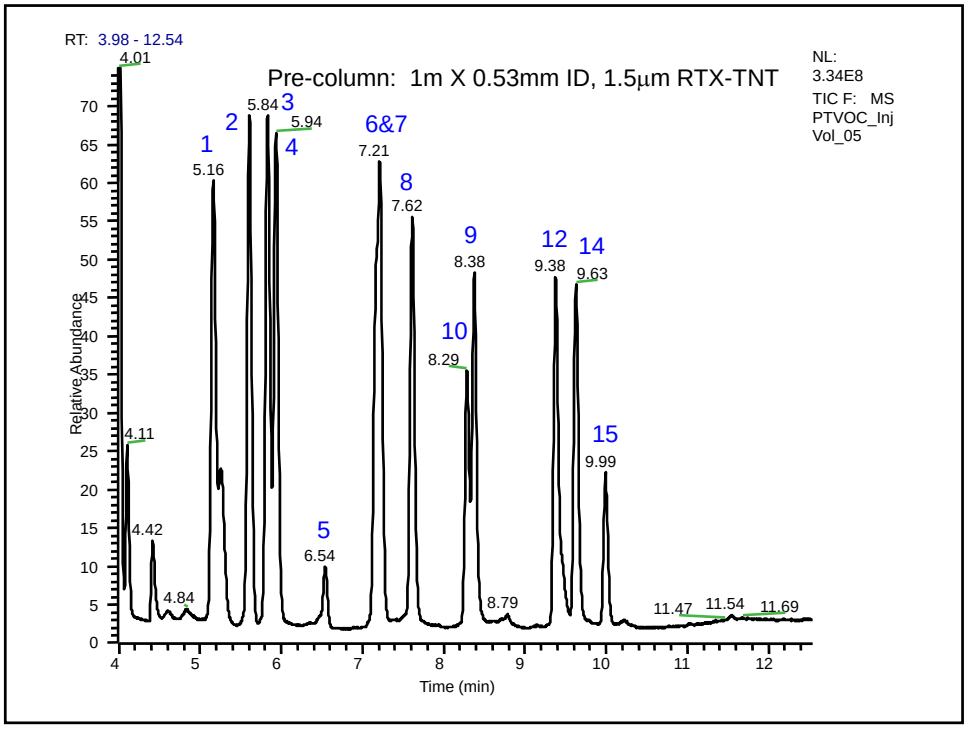
Pre-column Study

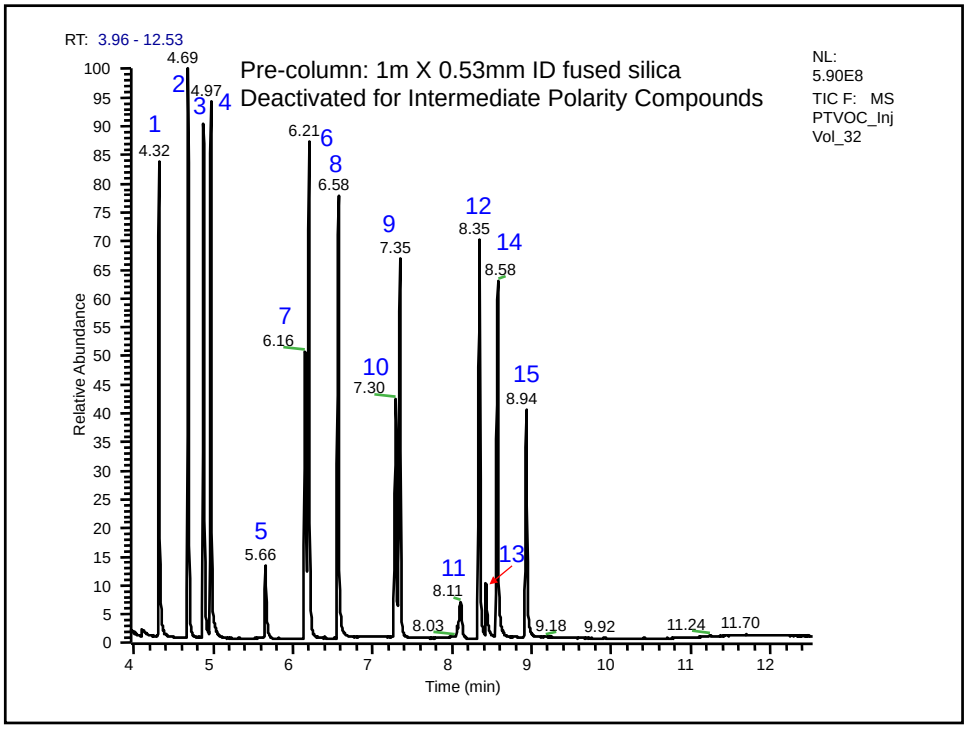
- Examination of Pre-column phase thickness for RTX-5 pre-columns
- Examination of RTX-TNT as a pre-column
- Examination of deactivated, un-coated fused silica as pre-column




RT: 3.98 - 12.53
Pre-column: 1m X 0.53mm ID, 1.0µm RTX-5
NL:
1.21E8
TIC F: MS
ExplPreCol_
13
Relative Abundance
Time (min)
1 4.98
2 5.41
3 5.62
4 5.73
5 6.39
6
7 6.99
8 7.41
9 8.18
10 8.13
11
12 9.20
13
14 9.44
15 9.80
4.18
8.02
8.58
9.03
9.96
11.57
11.65


RT: 3.98 - 12.46
Pre-column: 1m X 0.53mm, 0.5µm RTX-5
NL:
4.71E8
TIC F: MS
ExplPreCol_
02
Relative Abundance
Time (min)
1 4.31
2 4.68
3 4.88
4 4.97
5 5.65
6 6.20
7 6.15
8 6.57
9 7.34
10 7.29
11 8.09
12 8.34
13
14 8.57
15 8.93
6.93
8.04
9.11
9.65
11.31
11.70
12.09


RT: 3.98 - 12.54
Pre-column: 1m X 0.53mm ID, 1.5µm RTX-TNT
NL:
3.34E8
TIC F: MS
PTVOC_Inj
Vol_05
Relative Abundance
Time (min)
4.01
4.11
4.42
4.84
5.16
5.84
5.94
6.54
7.21
7.62
8.29
8.38
8.79
9.38
9.63
9.99
11.47
11.54
11.69
1
2
3
4
5
6&7
8
9
10
12
14
15


RT: 3.96 - 12.53
Pre-column: 1m X 0.53mm ID fused silica
Deactivated for Intermediate Polarity Compounds
NL:
5.90E8
TIC F: MS
PTVOC_Inj
Vol_32
Relative Abundance
Time (min)
4.32
4.69
4.97
5.66
6.16
6.21
6.58
7.30
7.35
8.03
8.11
8.35
8.58
8.94
9.18
9.92
11.24
11.70
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

Pre-column Study

Results

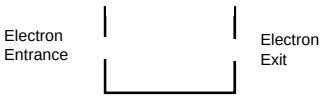
- Coated pre-columns with thicker coatings tended to distort the chromatogram and lose resolution
- Pre-columns without coating or coated with thin (0.5mm) coating produced better resolution and less peak broadening

Chemical Ionization

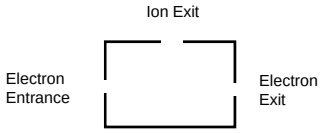
- Chemical ionization was performed using methane as the reagent/moderator gas
- Investigated positive vs. negative chemical ionization
- Trace-DSQ was equipped with 2 types of ion volume for CI conditions, labeled as CI ion volumes and EI/CI ion volumes

Ion Volumes

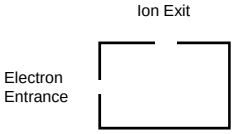
Sketches, Not to Scale



EI Ion Volume

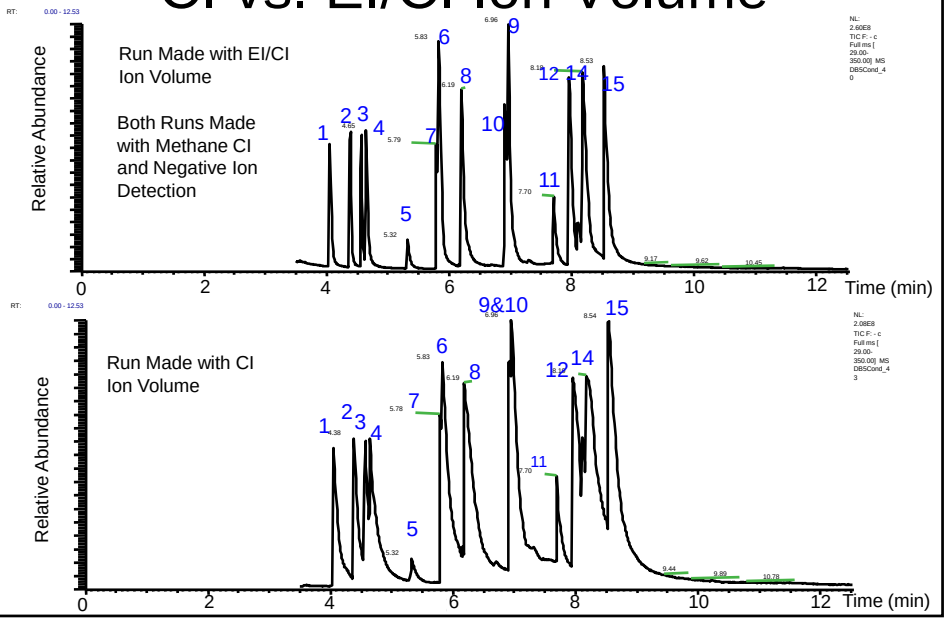


EI/CI Ion Volume



CI Ion Volume

CI vs. EI/CI Ion Volume



EI vs. EI/CI Ion Volume

- EI/CI ion volume produces narrower or “sharper” peaks, although less so than a simple EI ion volume
- Our conclusion is that the additional gas exchange permitted by the EI/CI ion source allows the sample material to exit the ion source more readily and eliminates tailing due to poor detector flushing.

Summary

- HMX was present in the standards but was never seen
- PETN was present in the standards, but it was detected poorly, if at all

Conclusions

- Un-coated or thinly coated pre-columns better preserve the chromatographic resolution
- Our column and pre-column arrangements favored restricted sample sizes for simile on-column injections
- Chromatographic resolution appears to be decreased when using “tighter” ion volumes
- CI conditions force a compromise between open and tight ion source

Acknowledgement: This project was carried out as an in-house project of the Air Force Research Laboratory.

Disclaimer: Certain instruments, accessories, and software have been named in effort to fully document the procedures followed. Such mention does not imply recommendation or endorsement by the Air Force nor does it imply that the items identified are the best available for the purpose.

Release: This poster has been reviewed by Public Affairs and is approved for public release.

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